

Van der Waals energy surface of carbon nanotubes sheet

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The van der Waals interaction between a carbon nanotubes sheet (CNTS) and a rare gas atom, is studied using both atomistic and continuum approaches. We present analytical expressions for the van der Waals energy of continuous nanotubes interacting with a rare gas atom. It is found that the continuum approach does not properly treat the effect of atomistic configurations on the energy surfaces. The energy barriers are small as compared to the thermal energy, which implies the free motion above the CNTS in heights about one nanometer. In contrast to the energy surface of a graphene sheet, the honeycomb lattice structure in the energy surface of a CNTS is imperceivable. Defects alter the energy surface which therefore influence the gas absorption mechanism.

I. INTRODUCTION

In the past two decades, various properties of carbon nanotubes such as their unique structure and mechanical, chemical and electronic properties, have been attracted much attention [1]. Zhang *et al* used a solid state sheet fabrication technique and could synthesize highly oriented free standing carbon nanotubes sheets (CNTS) [2]. The produced CNTS combines high transparency with high electronic conductivity and are highly flexible and provide giant gravimetric surface areas. The long, high perfection nanotubes are needed to maximize the electrical and thermal conductivities and mechanical properties [2]. Recently Li *et al* [3] have fabricated highly engineered ultra-thin anisotropic single wall carbon nanotube films formed on three dimensional micro-patterned substrates. Therefore CNTS can be considered as a real multifunction sheet for the future technologies.

The two-dimensional structure of CNTS makes it possible to examine the possibility of the two-dimensional motion of an external particle over them [4, 5]. The absorption of rare gas on the CNTS can change the lattice parameter of nanotubes. In this regard Bienfait *et al* found experimentally the dilation of the apparent carbon nanotube bundle in the presence of argon gas atoms [5].

The potential energy surface (ES) of CNTS explains different motion-related phenomena at nanoscale as well as the various directed motions on the carbon nanotube-based motors [6, 7]. Since rare gas atoms are experimentally used to control temperature, pressure and other thermodynamical properties of nanoscale materials [8, 9], it is important to investigate the van der Waals (vdW) potential energy surface around a CNTS. Recently, we found a diffusive motion for the motion of C_{60} molecule over graphene sheet and depicted that the energy barriers are small as compared to the thermal energy [6]. By employing a different approach, i.e. Langevin dynamics, we showed that a rare gas over graphene sheet has a diffusive motion [10].

There are two common approaches for studying the various properties of carbon nanotubes based nanostructures: 1) atomistic and 2) continuum. Yakobson *et al* [11] have shown that the mechanics of carbon nanotubes

is interpretable using the continuum elasticity of shells. The pioneering work of Yakobson and co-workers made common practice of using of continuum models for simulations of mechanical properties of nanotubes [12–14]. In recent studies, it has been shown that atomistic and continuum approaches can be combined together to study mechanical behavior of different materials [12]. However, in the present study, we will show that employing of the continuum approach for energy based properties (but not elastic energy) is not appropriate.

In this study the ES of a CNTS due to the vdW interaction with a rare gas atom is investigated. We show that the ESs are periodic in the planes which are parallel to the CNTS layers. We find that there are significant differences between ES of the atomistic model and those predicted from the continuum model. The binding energies and the physical-bond distances obtained from the atomistic model differ from the continuum model. We conclude that the continuum model is inappropriate approach for energetic consideration and yields inaccurate results for the chemical absorption of atoms into the CNTS. However mechanics of atomistic systems (carbon nanotubes) greatly benefits from continuum mechanics [11, 12]. In addition, we have investigated the ES of graphene and compared it to the one obtained for CNTS. It is found that the honeycomb lattice feature, which is observed in the ES of graphene, does not appear in the ESs of CNTS. This is attributed to the large curvature of carbon nanotubes in the CNTS sheet

Results for the CNTS comprises the zigzag nanotubes differ from the CNTS made of other types of nanotube chiralities. From our barrier energy calculations, it is found that the barriers for the motion of the rare gas atom on a CNTS become shallow at positions away from the CNTS. Moreover, the components of the force are calculated and are compared to those obtained from the continuum model. We show that the simplest kind of defect (i.e. vacancy), destroys the periodicity of the ES and reduces the energy barriers.

This paper is organized as follows. In Sec. II and III the details of atomistic and continuum models are presented. Sec. IV contains main results including those for the energy surfaces, force calculation, numerical solution

for the equation of motion and the results for ES of the defected CNTS. In Sec. V the results are summarized.

II. THE ATOMISTIC MODEL

A CNTS comprises many layers which are stacked on top of each other and are along z -axis. Many aligned carbon nanotubes which are parallel to the y -axis construct each layer. The carbon-carbon bond length, a_0 , is 1.42 Å. In our model, the origin of the xyz Cartesian coordinate system is set to be at the center of the top layer. Carbon nanotubes form different types, which can be described by the chiral vector with two indexes (m, n) , where m and n are integers of the chiral vector equation $\vec{R} = m\vec{a}_1 + n\vec{a}_2$. Here \vec{a}_1 and \vec{a}_2 are two basic vectors of graphene lattice and are given by $\vec{a}_1 = \sqrt{3}a_0\hat{i}$ and $\vec{a}_2 = \sqrt{3}/2a_0\hat{i} + 3/2a_0\hat{j}$, respectively. If $m=0$, the nanotubes are called zigzag (ZZ). If $n = m$, the nanotubes are called armchair (AC). Otherwise, they are called chiral (CR). The radius of a carbon nanotube with (m, n) indexes is given by $R_{m,n} = \frac{\sqrt{3}a_0}{2\pi}\sqrt{m^2 + n^2 + mn}$.

Figure 1(a) depicts eight aligned (5,5) carbon nanotubes from the top layer. Graphene is a planar structure made of carbon with one-atom thickness, where each carbon atoms have sp^2 hybridization with their neighboring atoms and are densely packed in a honeycomb crystal lattice. Carbon nanotubes can be formed by rolling up graphene sheets. In order to study the van der Waals interaction between an argon atom and a CNTS, we have employed the Lennard-Jones (LJ) potential. The LJ potential provides both the repulsive and attractive nature of the interaction between an uncharged noble gas and each atom of the CNTS. The LJ potential is the widely used potential in various simulations [15] for two interacting uncharged particles, i.e. $u(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)$, where r is the distance between two atoms, ϵ is the depth of the potential well, and σ is the distance at which the potential becomes zero. To model the interaction between two different types of atoms such as carbon and argon, we adjust LJ parameters using the equations $\epsilon = \sqrt{\epsilon_1\epsilon_2}$ and $\sigma = \frac{\sigma_1 + \sigma_2}{2}$. We use the parameters of carbon and argon atoms as $\sigma_1 = 3.369$ Å, $\epsilon_1 = 2.63$ meV, $\sigma_2 = 3.405$ Å and $\epsilon_2 = 10.23$ meV, respectively.

Total potential energy stored between an argon atom and a CNTS is written as the sum over all contributions of the carbon nanotubes in each layer,

$$E_T(x, y, z) = 4\epsilon \sum_{i=-N/2}^{N/2} \sum_{t=0}^{K-1} \sum_{j=1}^M \sum_{l=1}^2 (-1)^{l+1} \left(\frac{\sigma}{\delta r}\right)^{12/l}, \quad (1)$$

where $\delta r = |\vec{r} - (\vec{r}_{j,t}^i - tD\hat{k})|$ and $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$ refer to the position of the argon atom and $\vec{r}_{j,t}^i$ is the position vector of j^{th} carbon atom in the i^{th} carbon nanotube (of the t^{th} layer). Each nanotube has M atoms and the total number of carbon nanotubes in each layer

is $N + 1$. The sum over l also, is written for varying of the powers between 12 or 6. The sum over t counts the number of layers (K is the total number of layers) in different height along z -axis, such that each layer is separated by D from its neighboring layer. Note that each layer is shifted along the x -axis with respect to its top and bottom neighbors, i.e. $\vec{r}_{j,t+1}^i = \vec{r}_{j,t}^i \pm \frac{d}{2}\hat{i}$ where d is the lateral distance between tubes in each layer, see Fig. 1. In the CNTS having many layers, we show that the main contribution of the energy comes from the top layer, thus setting $K = 1$ would be a good approximation. We will prove this effect in Sec. IV-A (henceforth we set $K = 1$). Note that the potential energy in Eq. (1) is periodic along x -axis at fix z independent of the chirality and z , but the periodicity along y -axis depends on the chirality, i.e. $E_T(x, y, z) = E_T(x + \mu d, y + \nu \delta_{m,n}, z)$ where μ and ν are two integer numbers and $\delta_{m,n}$ is the periodicity number along y -axis, e.g. $\delta_{5,5} \cong \sqrt{3}a_0$ and $\delta_{9,0} \cong 3a_0$. In fact, the periodicity of the ES is a consequence of the crystalline structure and parallel alignment of the carbon nanotubes. Moreover, the gas absorption into the CNTS depends on the ES periodic structure.

The gradient of the potential is the force experienced by the argon atom

$$\vec{F} = 48\epsilon \sum_{i=-N/2}^{N/2} \sum_{t=0}^{K-1} \sum_{j=1}^M \sum_{l=1}^2 \frac{(-1)^{l+2} \delta \vec{r}}{l \delta r^2} \left(\frac{\sigma}{\delta r}\right)^{12/l}. \quad (2)$$

Newton's second law should be solved numerically for determining the path of the motion.

III. THE CONTINUUM MODEL

Considering a hollow and continuous cylinder as a simple model for the carbon nanotube [16] is the main assumption for the continuum approach. Again, $N+1$ aligned tubes along y -axis are separated by the distance d in each layer of CNTS. The obvious difference between the atomistic model and the continuum model is the absence of the chirality effect in the continuum model. The other important difference is the periodicity of ES along y -axis in the atomistic model (not in the continuum model) which will be discussed further in the next section. The LJ potential energy for $N+1$ cylinders which are interacting with a rare gas atom and are parallel and aligned along the y -axis (when $K = 1$) is

$$E_C(x, y, z) = \sum_{i=-N/2}^{N/2} E_i(x, y, z), \quad (3)$$

where $E_i(x, y, z)$ is the contribution of the i^{th} nanotube and is given by

$$E_i(x, y, z) = \sum_{l=1}^2 \int_0^{2\pi} \int_0^L \frac{2 n_l (-1)^{l+1} R_{n,m} d\phi dy_i}{[\Re_i^2 - 2 \sin(\phi_i) + (y - y_i)^2]^{6/l}}, \quad (4)$$

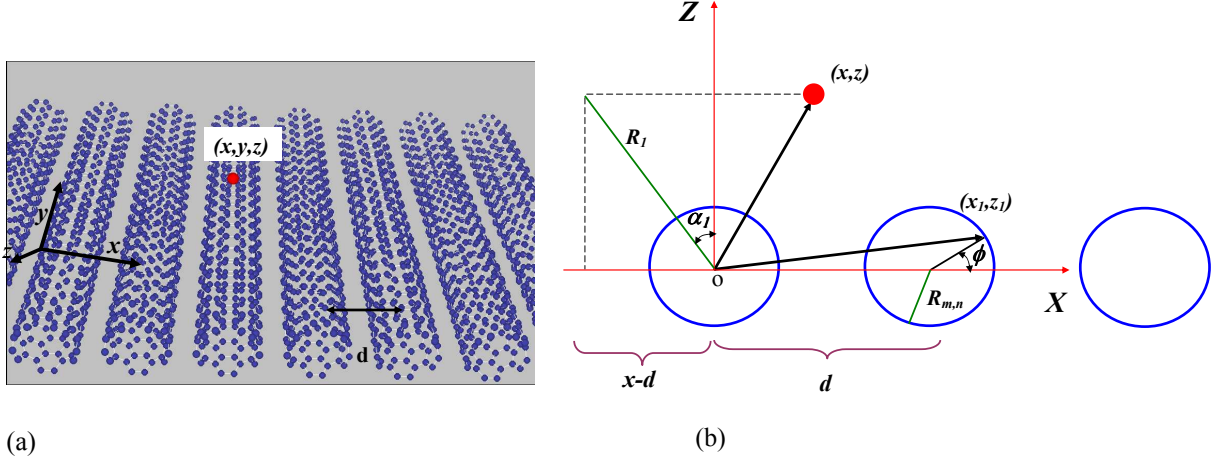


FIG. 1: (Color online) (a) The atomistic model of a CNTS. The top layer of an AC-CNTS comprises eight nanotubes with $M = 400$ and $d = 10 \text{ \AA}$. (b) The continuum model of a CNTS. The front view of three continuous tubes with the relevant variables for Eq. (4). The red sphere is an argon atom located at (x, y, z) position.

with $n_l = 4\epsilon\sigma^{12/l}\Sigma$ where Σ is the mean surface density of carbon atoms for a graphene lattice which is $\Sigma = \frac{2}{|\vec{a}_1 \times \vec{a}_2|}$. In Eq. (4) (x_i, y_i, z_i) is the coordinates of the chosen element from the i^{th} nanotube, L is an arbitrary length, $R_{n,m}^2 = x_i^2 + z_i^2$ is the radius of each nanotube, $\alpha_i = \tan^{-1}(\frac{x+i d}{z})$, $\varphi_i = \phi + \alpha_i$, $\mathfrak{R}_i^2 = R_{m,n}^2 + R_i^2$, $R_i^2 = (x + i d)^2 + z^2$. Note that “ i ” is a positive integer number where $x_i < 0$ and vice versa. In Fig. 1(b) we illustrate the front view (in $x - z$ plane) of only three

nanotubes from the top layer. The relevant variables for the model are exhibited in Fig. 1(b). The following integrals are taken over the middle nanotube referring to $i = 1$ in Eq. (4).

The integrals over the longitudinal viable (y_i for the i^{th} cylinder) are done analytically and the integrals over the azimuthal angle (ϕ) are obtained numerically by employing Mathematica software. The result of the integration over y_i for repulsive term is

$$I_R(x, y, z, \phi) = \int_0^L \frac{n_1 dy_i}{(A + (y - y_i)^2)^6}$$

$$= \frac{n_1 \left(\sqrt{A} \zeta (965A^4 + 2370A^3\zeta^2 + 2688A^2\zeta^4 + 1470A\zeta^6 + 315\zeta^8) + 315(A + \zeta^2)^5 \text{ArcTan} \left[\frac{\zeta}{\sqrt{A}} \right] \right)}{1280A^{11/2}(A + \zeta^2)^5},$$

and for attractive term is

$$I_A(x, y, z, \phi) = \int_0^L \frac{-n_2 dy_i}{(A + (y - y_i)^2)^3} = -\frac{n_2 \zeta (5A + 3\zeta^2)}{8A^2(A + \zeta^2)^2} - \frac{3n_2 \text{ArcTan} \left[\frac{\zeta}{\sqrt{A}} \right]}{8A^{5/2}},$$

where $A = \mathfrak{R}_i^2 - 2 \sin(\varphi_i)$ and $\zeta = y - y_i$. Combining two above integrals, the continuum model energy is written as

$$E_C(x, y, z) = \sum_{i=-N/2}^{N/2} \int_0^{2\pi} 2 R_{n,m} (I_R(x, y, z, \phi) + I_A(x, y, z, \phi)) \Big|_{y_i=0}^{y_i=L} d\phi.$$

Differentiating the above equation gives the force ex-

perienced by the argon atom due the interaction with i^{th}

tube:

$$\vec{F}_i = \sum_{l=1}^2 \int_0^{2\pi} \int_0^L \frac{24 \vec{\Delta r} n_l (-1)^{l+1} R_{n,m} d\phi dy_i}{l [\mathcal{R}_i^2 - 2 \sin(\varphi_i) + (y - y_i)^2]^{6/l+1}}, \quad (5)$$

where $\vec{\Delta r} = (x + id - x_i)\hat{i} + (y - y_i)\hat{j} + (z - z_i)\hat{k}$.

We will compare the results of the continuum model with those of the atomistic model in the next section.

IV. RESULTS AND DISCUSSIONS

A. Energy surface

Figure 2 shows two energy surfaces (ES) in the $x - y$ plane above the CNTS at $z = 6.5 \text{ \AA}$ which are related to the atomistic (Eq. (1)) and the continuum (Eq. (3)) models, i.e. $E_T(x, y, 6.5 \text{ \AA})$ and $E_C(x, y, 6.5 \text{ \AA})$ respectively. The ESs were calculated with $K=1$, $N=7$ and $d=10 \text{ \AA}$ (these are fixed in this study). For the atomistic model (Fig. 2(a)) we set $M = 400$ for AC nanotubes with (5,5) indexes. The colored tubes indicate the location of the top layer of the CNTS (includes eight aligned carbon nanotubes). We found that the chosen values for M and N are sufficiently large to eliminate boundaries when ES is considered in the range of $|x, y| < 20 \text{ \AA}$. In contrast to the ES obtained for the graphene [6], from the ES in Fig. 2(a) one can not identify the honeycomb lattice structure of the nanotubes. This is because of the curvature of the nanotubes. Moreover, the ES approaches to a flat surface far away from the sheet.

As can be seen from Fig. 2, the main difference between two models is the appearance of the periodic peaks along y -axis in the atomistic model. In spite of the continuum energy surface, i.e. E_C , E_T has many peaks/valleys along the y -axis (above (id, y) points for each integer 'i'). These valleys make the connection between two adjacent channels easier and will also enhance the probability of the lateral motion (along x -axis) of the particle through the mentioned valleys. Furthermore the appearance of the peaks along the $x = id/2$ line can be understood regarding to the closed energy curves around a single nanotube (Fig. 8(a)) in the $x - z$ plane. Assume two such nanotubes get laterally closer from infinite distances. At certain distances due to the overlap of their energy curves, the mentioned peaks appear.

We depict ES of ZZ-CNTS with (9,0) indexes and CR-CNTS with (6,4) indexes in Fig. 3 (we used shorthand letters ZZ, AC and CR for ZZ-CNTS, AC-CNTS and CR-CNTS, respectively in the figures legends). Note that $R_{9,0} \approx R_{6,4} \cong R_{5,5} = 3.39 \text{ \AA}$ and that is the reason for choosing (9,0) and (6,4) indexes. It is clear from Fig. 3 that the periodicity of E_T along y -axis depends on the (m, n) indexes.

Increasing the number of layers, i.e. K , varies ES slightly implying that the major part of the ES is due to the interaction with the top layer. In order to prove this fact, we show the variation of E_T for AC-CNTS

with $K=3$ and $K=1$ versus z in Fig. 4. The ratio $E_T|_{K=3}/E_T|_{K=1}$ varies around one, thus setting $K=1$ is a reasonable assumption. The same behaviors were obtained for the variations of the mentioned ratio versus x and y .

Figure 5 shows the variation of ES for an AC-CNTS along z -axis at different (x, y) points, namely $E_T(0, 0, z)$, $E_T(d/2, 0, z)$ and $E_C(0, 0, z)$, $E_C(d/2, 0, z)$. Although these curves are similar to $u(r)$ function, but indeed they are different. The curves for ZZ-CNTS have different minima as compared to those for AC-CNTS and CR-CNTS. The minimum of energy curve for ZZ-CNTS (above $(x = 0, y = 0)$ point) is around $6.99 \text{ \AA} - R_{9,0}$ and is about $6.75 \text{ \AA} - R_{5,5}$ for AC-CNTS and CR-CNTS. The lowest energy occurs for E_C . In general, the energy curves above $(id/2, y)$ points have a shift with respect to those above (id, y) , see Fig. 5. The appearance of the minima above $(id/2, y)$ points are apparently in contrast to the appearance of the ES's peaks above the same points in Fig. 2 and Fig. 3. In fact, this is an unpredictable effect that when z decreases, the energy increases above (id, y) and decreases above the points between the tubes (i.e. $(id/2, y)$) independent of the y values. Above $(id/2, y)$ points the minima are due to the free space between adjacent tubes, i.e. the grooves between two adjacent nanotubes. Therefore the particles will prefer to aggregate between the tubes than above the tubes. Notice that above $(id/2, 0)$ points the binding energy (minima of the curves) is almost twice smaller than the one above $(id, 0)$. The minima of the curves above $(0, 0)$ are around 70 meV and above $(id/2, 0)$ points are about 128 meV which are 2.7 and 4.9 times larger than the thermal energy at room temperature, respectively. The binding energy of an argon atom above a graphene sheet is around $\simeq 85 \text{ meV}$ [10], which is smaller than the binding energy of an argon atom located at $(id/2, 0)$ above a CNTS.

To investigate the periodicity of energy along x and y -axis the variations of ES are shown in Fig. 6. Notice that the variations of energy versus x are almost the same for AC, CR and E_C while they are different from ZZ. In all cases the minima of the curves are equal, independent of the chirality and z values. Figure 6(b) shows the variations of energy versus y at $z = 6.5 \text{ \AA}$. In spite of the curves in Fig. 6(a), the periodicity along y depends on the chirality. The E_C is a constant along y -axis.

The maximum barriers are found for ZZ-CNTS and the minimum are for AC-CNTS. The barriers in the CR-CNTS vary with y resulting the possibility of the absorption of external atoms in different energy levels. However, the barriers in the AC-CNTS are constant for fixed z , which are consequence of the sine shape of the curves. Figure 6(c) shows the variation of the energy barriers ($\delta = E_{max} - E_{min}$) versus z in log-log scales. The barriers decrease non-linearly with z which implies that far from the sheet, the particle has free-like motion.

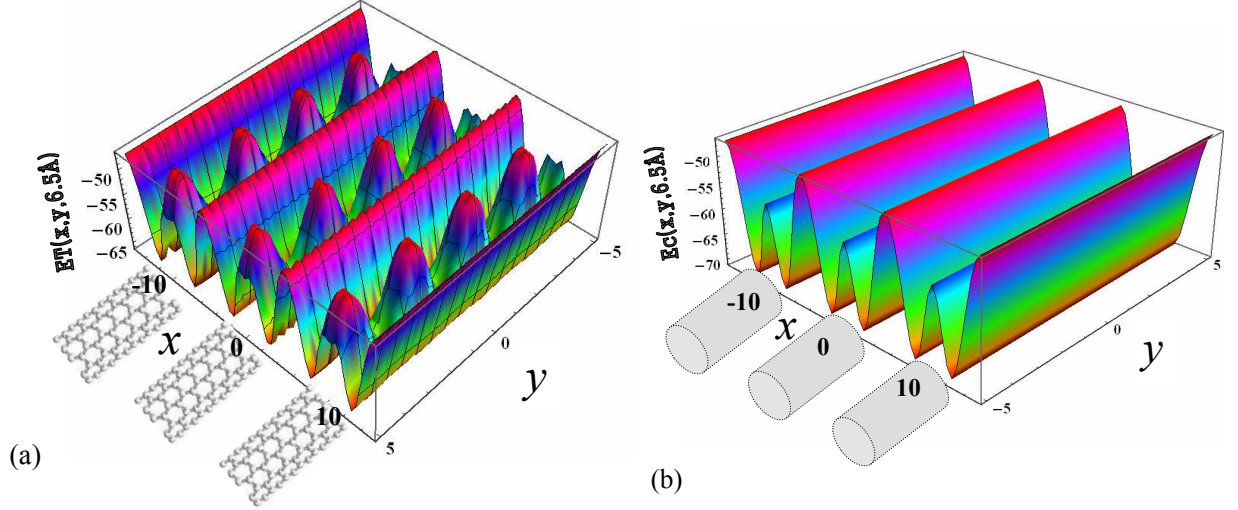


FIG. 2: (Color online) (a) The vdW energy surface of a CNTS comprises of aligned armchair nanotubes interacting with an argon atom (located at $z = 6.5 \text{ \AA}$). (b) The vdW energy surface of continuous tubes interacting with an argon atom (located at $z = 6.5 \text{ \AA}$).

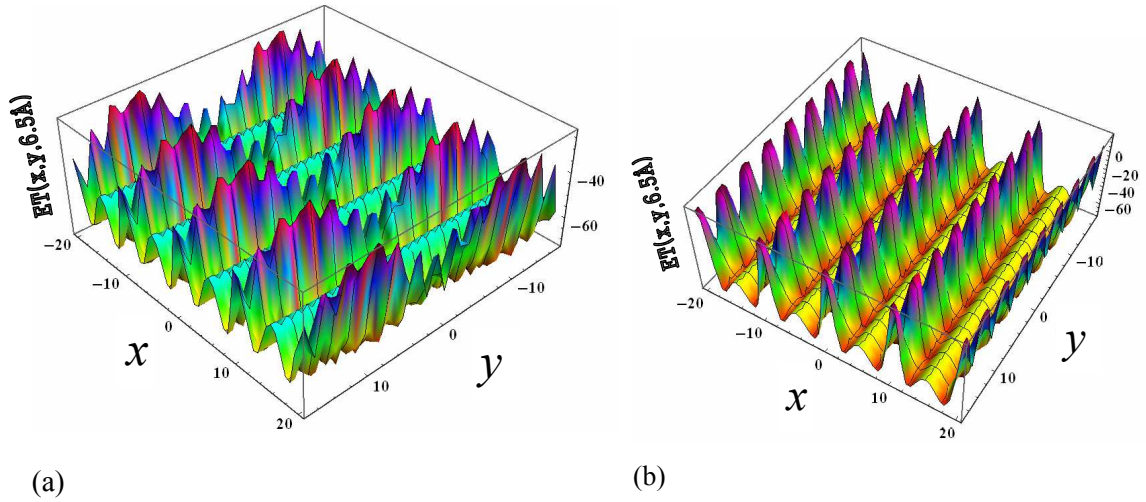


FIG. 3: (Color online) The vdW energy surface of chiral nanotubes with (6,4) indexes in (a) and zigzag nanotubes with (9,0) indexes in (b), which are interacting with an argon atom (located at $z = 6.5 \text{ \AA}$).

B. Force calculations

Using Eq. (2) and Eq. (5) we calculated the various components of the force experienced by an atom above CNTSs with different chiralities. Here we report the variation of F_z versus z , F_x versus x and F_y versus y . Figure 7(a) shows the variation of the F_z versus z at two points (0,0) and $(d/2,0)$. Clearly the ZZ-CNTS attracts particle differently. The forces on the argon atom at $(i d/2,0)$ point is more attractive than the one at $(i d,0)$ implying tendency of the particles to aggregate between the tubes.

Figure 7(b) shows the variation of the F_x versus x for various y at $z = 6.5 \text{ \AA}$. As we see the curves for the AC-CNTS and the CR-CNTS are similar. Figure 7(c) shows the variation of the F_y for an AC-CNTS versus y for different x and $z = 6.5 \text{ \AA}$. The absolute values of the forces decrease with increasing x .

C. Equations of motion

In order to find the path of the motion of an argon atom above the CNTS, we solved equations of mo-

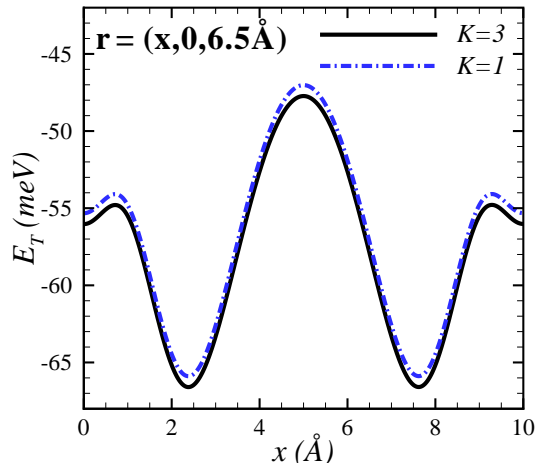


FIG. 4: (Color online) Comparison of the energy curves (as a function of x) produced by three layers of AC-CNTS (solid curve) and by one layer of AC-CNTS (dashed curve) for $y = 0$ and $z = 6.5 \text{ \AA}$.

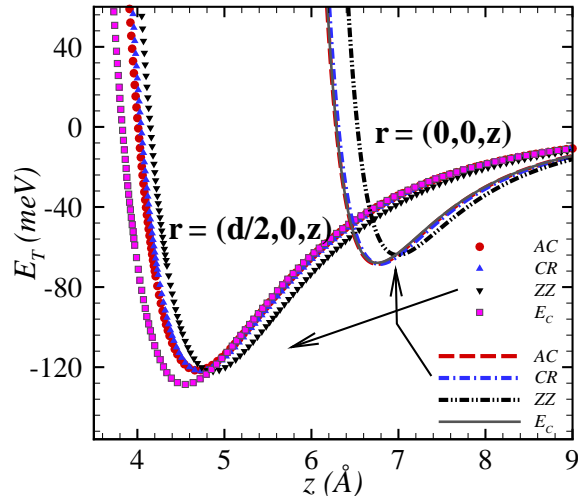


FIG. 5: (Color online) Variation of the energy versus z for different type of carbon nanotube sheets above two points $(0, 0)$ and $(d/2, 0)$ in the $x - y$ plane.

tion numerically. The aim is to find the influence of the ES on the path of motion of an external atom. The study of an argon atom close to a single nanotube surface provides further insights into the problem. Therefore it would be helpful to show how ES energy curves varies around an individual carbon nanotube. Figure 8(a) shows the energy curves for three z values, i.e. $z = 6.25 \text{ \AA}$, 6.5 \AA , 6.75 \AA , 7 \AA . These cycloidal closed curves have been obtained by transforming the Cartesian coordinates (in Eq. (1)) to the polar coordinates. It is observed that with increasing z , the curves close to

the circular shape which results in the flattening of ES at distances far away from the sheet

The numerical solutions is presented for both the motion of an argon atom around an individual AC carbon nanotube and an AC-CNT. The velocity Verlet algorithm is used for the numerical integration and the time is step set to be 1 fs. To solve the Newton's equation one needs two initial conditions, namely the initial position of the argon atom and its initial velocity. We set the initial position to $(0, 0, 6.5 \text{ \AA})$ and the velocity vector to an arbitrary vector $\vec{v} = (v_x, v_y, v_z)$. We found that the larger initial velocities (corresponds to the higher kinetic energy of the atom) give the larger probability for passing the barriers. Figure 8(b) shows the front view of the two typical paths with $\vec{v} = (3, 3, 3)$ and $\vec{v} = (5, 5, 5)$. It is also found that argon atoms with larger initial velocity, have larger fluctuation amplitude around the tubes.

In addition, we give the results for the path of the motion of an argon atom above an AC-CNTS. Figure 8(c) shows the front view of the resultant. Notice that the particle prefer to aggregate within the grooves. Increasing the initial velocity of the particle enables the particle to overcome the barriers and visit more points at higher heights. In Fig. 8(b) and Figure 8(c) the dashed inner circles indicate the carbon nanotubes locations.

D. Defected CNTS

Removing an atom from a perfect carbon nanotube makes CNTS defective. The ES varies in the presence of the defect. Defects changed the absorption mechanism and the paths of the motion of external atoms. Figure 9 shows the ES of an AC-CNTS (with (5,5) indexes) where vacant site was put in the middle of the central nanotube. Notice that the periodicity of the ES is altered around the vacancy. Vertical yellow arrow refers to the vacant site. We show the variation of $E_T(x, y, z)$ versus both x and y in Fig. 9(b). The solid curve corresponds to the variation versus x and the dashed curve is related to the variation versus y . Comparing these curves with those shown in Fig. 6(b,c) for perfect CNTS implies that the energy barriers are reduced due to the presence of the defect (gives more free motion along the x -direction). We have performed the same calculations for the CNTS with different chirality and found similar behaviors. Moreover, solving equations of motion in this case showed that the regular aggregation between and above the tubes is missed. Increasing the number of vacant sites causes aperiodic energy surfaces.

V. CONCLUSIONS

Both the atomistic and the continuum models were employed to study the van der Waals energy surface around a carbon nanotube sheet. The continuum model can not reveal the atomistic features of the problem. The car-

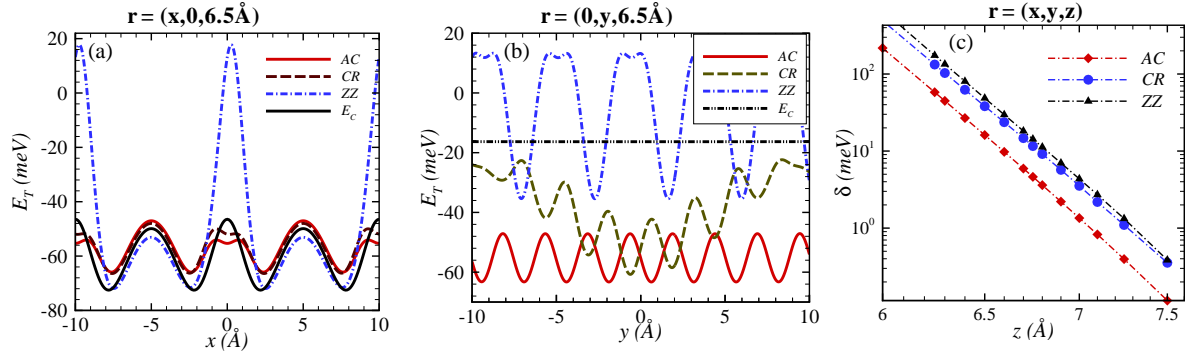


FIG. 6: (Color online) The periodic vdW potential energy versus x for $(x, 0, 6.5 \text{ Å})$ in (a) and versus y for $(0, y, 6.5 \text{ Å})$ in (b). (c) Variation of the energy barriers ($\delta = E_{max}(x, y, z) - E_{min}(x, y, z)$) along z .

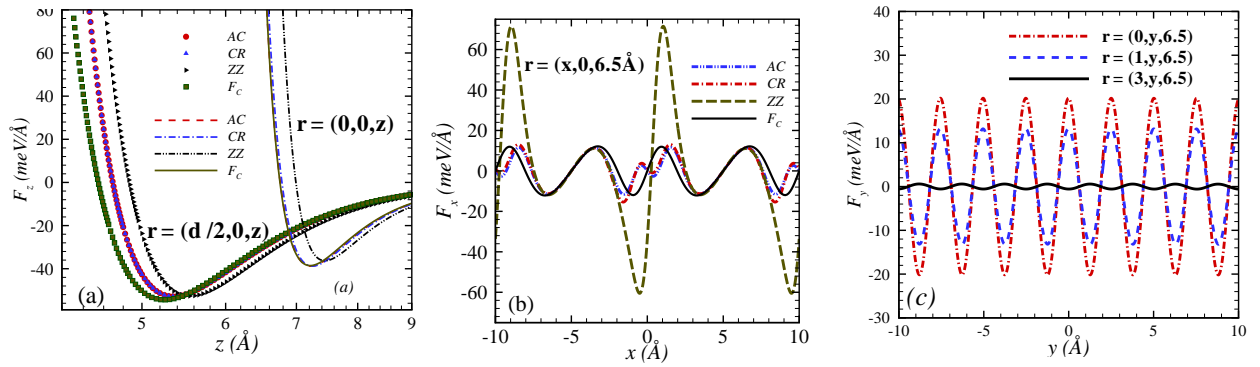


FIG. 7: (Color online) (a) Variation of the z -component of the force versus z which is acting on an argon atom located above $(0, 0)$ point. (b) Variation of the x -component of the force versus x which is acting on an argon atom located at $(x, 0, 6.5 \text{ Å})$. (c) Variation of the y -component of the force versus y which is acting on an argon atom located at $(0, y, 6.5 \text{ Å})$, $(1, y, 6.5 \text{ Å})$ and $(3, y, 6.5 \text{ Å})$.

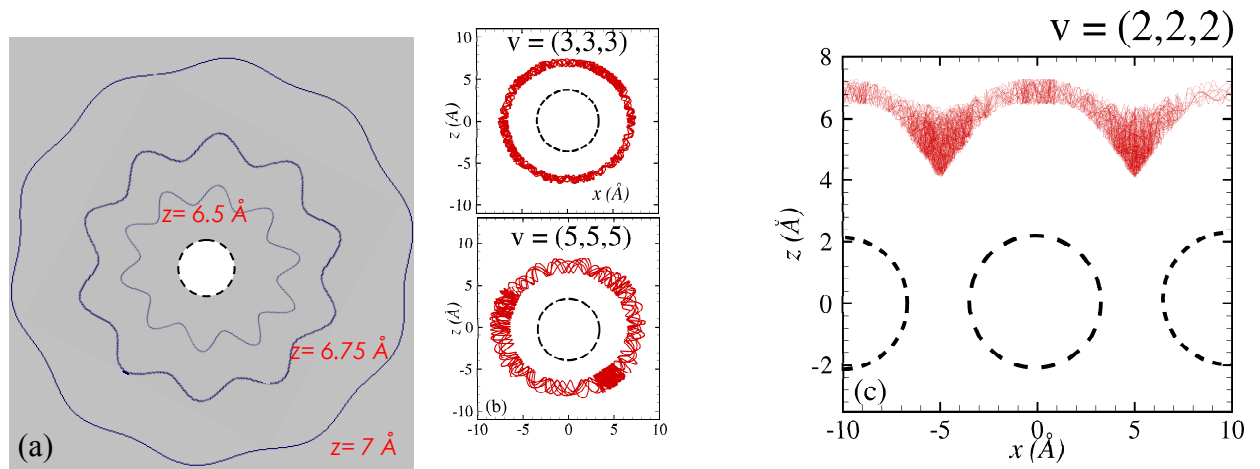


FIG. 8: (Color online) (a) Front view of the energy curves at various heights (b) and the path of the motion of an argon atom (with two different initial velocities) around an armchair nanotube. (c) The path of the motion of an argon atom with initial velocity $(2, 2, 2)$ in semispace above a CNTS.

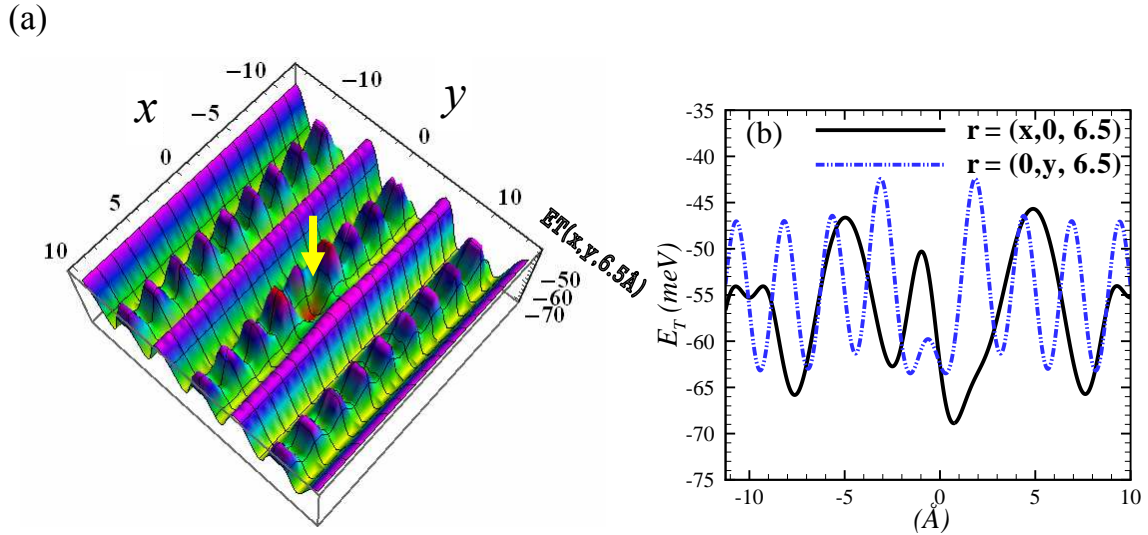


FIG. 9: (Color online) (a) Energy surface for an AC CNTS with a vacancy in the center of the middle tube. The yellow vertical arrow indicates the vacant site. (b) The variation of the energy versus x and y , respectively. For the dashed curve $x=0$ and for the solid curve $y=0$ for $z = 6.5 \text{ \AA}$.

bon nanotube sheet comprises zigzag carbon nanotubes, shows different periodicity in the energy surface as compared to those obtained from armchair and chiral carbon nanotube sheets. The equation of motion was solved numerically and the path of the motion of a rare gas atom moving within the energy surface was determined.

The continuum model predicts the constant energy along tubes axes which is in contrast to the results obtained from the atomistic model. The energy barriers decrease rapidly with height. Defects disturb the periodicity of the energy surface, reduce the barriers and change the gas absorption mechanism.

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